

Article

Kinetic Analysis of Boron and Phosphorus Removal from Si-Fe Alloy by CaO-Al₂O₃-SiO₂-Na₂O Slag

Golam Ismot Ara Taposhe ^{1,*}  and Leili Tafaghodi Khajavi ² 

¹ Department of Materials Engineering, University of British Columbia, Vancouver, BC V6T 1Z4, Canada

² Department of Materials Science and Engineering, McMaster University, Hamilton, ON L8S 4L7, Canada; tafaghodi@mcmaster.ca

* Correspondence: taposhe@mail.ubc.ca

Abstract: A hybrid process of slag and solvent refining was used to remove boron and phosphorus from silicon. Quaternary slag of CaO-Al₂O₃-SiO₂-Na₂O was employed to remove boron (B) and phosphorus (P) from Si-20 wt% Fe alloy at 1300 °C. A slag-to-metal ratio of one was used at different reaction times. The mass transfer coefficient of B and P in the slag and alloy phases was calculated to determine the rate-limiting step. The mass transfer coefficients of B in the alloy and slag phases were $6.6 \times 10^{-7} \text{ ms}^{-1}$ and $2.8 \times 10^{-7} \text{ ms}^{-1}$, respectively. The mass transfer coefficients of P in the alloy and slag phases were determined to be $7.5 \times 10^{-8} \text{ ms}^{-1}$ and $3.5 \times 10^{-7} \text{ ms}^{-1}$, respectively. The rate-limiting stage of the slag-alloy reaction kinetics was mass transport in the liquid slag for B and mass transport in the alloy phase for P.

Keywords: silicon; boron; phosphorus; slag refining; kinetics



Citation: Taposhe, G.I.A.; Khajavi, L.T. Kinetic Analysis of Boron and Phosphorus Removal from Si-Fe Alloy by CaO-Al₂O₃-SiO₂-Na₂O Slag. *Processes* **2023**, *11*, 2065. <https://doi.org/10.3390/pr11072065>

Academic Editor: Prashant K. Sarswat

Received: 9 May 2023

Revised: 4 July 2023

Accepted: 6 July 2023

Published: 11 July 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Ultra-pure silicon (9 N) for electronic applications is produced by chemical vapor deposition techniques such as the Siemens method. Considering the high energy intensity of these processes and the difference in silicon purity required for application in micro-electronics and in photovoltaics (6–7 N), developing processes for the mass production of silicon for photovoltaic applications has been the subject of much investigation [1–5]. Metallurgical techniques have been particularly focused on because of their scalability. Slag refining is one of the metallurgical processes applicable to Si purification. Slag refining involves the oxidation and dissolution of impurities in the slag phase. For example, B oxidizes to form borate, and P oxidizes to produce phosphate or phosphide. Later, these oxides dissolve in slag. Several investigations were carried out on binary slags, such as SiO₂-CaO [6], SiO₂-MgO [7], and SiO₂-Na₂O [8], ternary slags, such as CaO-SiO₂-CaCl₂ [9], CaO-SiO₂-MgO, and SiO₂-Al₂O₃-MgO [2], and quaternary slags like CaO-SiO₂-Al₂O₃-MgO [2] and CaO-SiO₂-Al₂O₃-CaF₂ [10]. However, the removal of B and P is still one of the main challenges in the slag refining of Si. Solvent refining involves alloying silicon with a metal that has a higher affinity for B and P compared to the affinity of silicon for B and P. Alloying metals like Al [11–15], Cu [16,17], and Fe [18–20] were examined by previous researchers. Even though these metals could remove B and P to various degrees, a suitable concentration of impurities for solar applications is yet to be achieved [21]. Therefore, a hybrid process including slag and solvent refining is proposed to facilitate B and P removal. The process involves using slag to remove B and P from a silicon alloy, followed by controlled cooling to obtain high-purity silicon phases while leaving the residual B and P in the alloy phase.

Understanding the thermodynamics and kinetics of B and P distribution between the slag and alloy phases is crucial for process control. A significant number of investigations were carried out on the thermodynamic analysis of Si refining [18,19,22–28]. However, kinetic analysis on the mass transfer of B and P between the alloy and slag phases is

very limited. The kinetics of B mass transfer have been investigated using CaO-SiO₂ and CaO-SiO₂-MgO slags for refining Si-containing 250 ppm B [29]. The reaction temperature was between 1600 °C and 1650 °C. The mass transfer coefficient in CaO-SiO₂ slag was determined to be 1.2 and $2.1 \times 10^{-6} \text{ ms}^{-1}$ for the slag to Si ratios of 1 and 2, respectively. For CaO-SiO₂-MgO slag, the mass transfer coefficient was reported to be $3.2 \times 10^{-6} \text{ ms}^{-1}$. However, the rate-determining step was not determined in this study. Transport kinetics and equilibrium studies were carried out between ferrosilicon (Si-50–85 wt% Fe) doped with 300 ppm B and slag (CaO-SiO₂) with a variable reaction time at 1600 °C [30]. The B mass transfer coefficient value between the alloy and the slag phase was determined to be $1.43\text{--}1.8 \times 10^{-6} \text{ ms}^{-1}$ with the variable alloy composition in the range of 50–85 wt% Fe. The mass transfer rate of B between ferrosilicon and slag increased marginally with ferrosilicon iron concentration. The rate-limiting step was assumed to be the mass transfer in the slag phase because the viscosity of the ferrosilicon alloy is several orders of magnitude lower than that of the slag.

Kinetic analysis of B removal from Si metal was investigated with binary CaO-SiO₂ and ternary CaO-SiO₂-Al₂O₃ slags [31]. The mass transfer coefficients in the binary slag were $2.24 \times 10^{-6} \text{ ms}^{-1}$, $2.59 \times 10^{-6} \text{ ms}^{-1}$, and $2.82 \times 10^{-6} \text{ ms}^{-1}$ at 1500 °C, 1550 °C, and 1600 °C. For ternary slag of CaO-SiO₂-Al₂O₃, the mass transfer coefficients were determined to be $1.49 \times 10^{-6} \text{ ms}^{-1}$, $1.86 \times 10^{-6} \text{ ms}^{-1}$, and $2.13 \times 10^{-6} \text{ ms}^{-1}$. The mass transfer coefficient slightly decreased when the Al₂O₃ content of the slag was increased from 9.59 wt% to 15.9 wt%.

Different slag systems, namely, CaO-SiO₂-Al₂O₃-(CaF₂) and Na₂SiO₃-CaO-SiO₂, were used to refine Si containing an initial B concentration of 13–25 ppm. The refining process was carried out at 1800 °C [32]. The mass transfer coefficients in the above slag phases are 1.19×10^{-6} and $10.1 \times 10^{-6} \text{ ms}^{-1}$, respectively. It was also reported that the mass transfer in the slag phase was the rate-determining step. The CaO-SiO₂ binary slag was also employed to refine Si containing 300 ppm B at 1600 °C [33]. The mass transfer coefficient value was estimated at $1.4 \times 10^{-6} \text{ ms}^{-1}$. Using CaO-SiO₂-TiO₂ slag and Si-100 ppm B at 1600 °C [34] resulted in a mass transfer coefficient of $5.2 \times 10^{-6} \text{ ms}^{-1}$. The CaO-SiO₂-K₂CO₃ ternary mixture was employed to examine the kinetics of B removal from Si-22 ppmw B at 1600 °C [35]. The mass transfer coefficient was measured for various slag compositions. The maximum mass transfer coefficient reported was $25.2 \times 10^{-6} \text{ ms}^{-1}$. The mass transfer in the ternary slag was determined to be the rate-limiting step of boron transfer.

CaO-SiO₂-CaCl₂ was used to refine Si-3.6 ppm B at 1600 °C and 1650 °C [36]. At 1600 °C, the mass transfer coefficient value was found to be $5.2 \times 10^{-6} \text{ ms}^{-1}$, while at 1650 °C, the value was $6.6 \times 10^{-6} \text{ ms}^{-1}$. Kinetic analysis of B removal from Si-22 ppmw B was also performed with CaO-SiO₂ and CaO-SiO₂-K₂CO₃ slag at 1550 °C [37]. For CaO-SiO₂-K₂CO₃ slag, the mass transfer coefficient value was reported as $2.43 \times 10^{-5} \text{ ms}^{-1}$, which is significantly higher than the value of $3.16 \times 10^{-6} \text{ ms}^{-1}$ for CaO-SiO₂. It was reported that addition of K₂CO₃ results in higher B mass transport in the slag phase.

The Li₂O-SiO₂ binary slag was used to investigate removal kinetics from Si-8.6 ppm B at 1700 °C [38]. However, the mass transfer coefficient value was comparatively low, i.e., $2.3 \times 10^{-8} \text{ ms}^{-1}$ compared to the previous research. Similar to the other investigations, mass transfer in the slag phase was found to be the rate-limiting step.

With the final goal of determining the rate-limiting step, this manuscript examines the kinetics of B and P removal from Si-20 wt% Fe alloy by CaO-SiO₂-Al₂O₃-Na₂O quaternary slag. The refining process was carried out at 1300 °C, which is lower than the previous investigations. The lower refining temperature will contribute to the lower energy consumption of the process. The mass transfer coefficients of B and P in the slag and the alloy phase were determined. The rate-limiting step for B and P removal was determined from the experimental analysis.

2. Materials and Methods

2.1. Alloy Preparation

The master alloy was prepared with 80 wt% Si and 20 wt% Fe with the addition of B and P as impurities. The crucible containing 150 g of the powder mixture was first heated at 3.2 °C/min up to 600 °C, followed by heating up to 1600 °C at the rate of 1 °C/min in a vertical tube furnace. The sample was kept for 10 h to complete melting. Then, the temperature was decreased to 600 °C (at a rate of 1 °C/min) followed by further cooling to room temperature at the rate of 3.2 °C/min. The heating, melting, and cooling processes were carried out in an Ar environment. The master alloy was ground by a grinder. An amount of 5 g of the master alloy was taken to conduct each experiment. The initial B and P concentration of the alloy is important for performing the kinetic analysis. Therefore, the initial concentration of B and P in each sample was measured using ICP-OES (inductively coupled plasma optical emission spectrometry). The model of the equipment used in the current investigation was Varian 725-ES.

Prior to ICP-OES analysis, 0.1 g of the alloy was chemically digested with an acid mixture containing 2 mL H₂SO₄, 5 mL HNO₃, and a dropwise addition of HF. The initial concentration of B and P was measured 3 times to obtain reliable values.

2.2. Slag Preparation

The optimum composition for maximum removal of B and P from the Si-Fe alloy was determined by the authors and has been reported in previous publications [22,23]. The optimum impurity removal at 1300 °C was achieved at CaO/SiO₂ of 1.5, SiO₂/Al₂O₃ of 2, and 10 wt% Na₂O for the quaternary slag. Considering the previous findings, 45 wt% CaO-30 wt% SiO₂-15 wt% Al₂O₃-10 wt% Na₂O was chosen as the slag composition to examine B and P removal kinetics at 1300 °C. An amount of 5 g of slag was premelted in an alumina crucible for 4 h at 1600 °C. The heating and cooling rates were similar to that of the alloy. The Ar atmosphere was maintained in the vertical tube furnace throughout the slag preparation process.

2.3. Experimental Procedure

The schematic and physical image of the tube furnace and the experimental setup are shown in Figure 1. Considering the 1:1 alloy to slag ratio, 5 g of the master alloy was added to 5 g of the premelted slag in the alumina crucible. The alumina crucible was placed in a graphite crucible and suspended from the upper cap of the furnace. The sample was heated at 3.2 °C/min to 600 °C/min, followed by 1 °C/min to 1500 °C, and kept at 1500 °C for 2 h. Later, the sample was cooled to 1300 °C at the rate of 1 °C/min. The reaction temperature was 1300 °C, while the reaction time was varied between 2 and 8 h for kinetic investigations. After the selected reaction time, the lower cap was opened, and the lower refractory plug was pulled out. The entire sample was quenched in a bucket of water which was placed under the furnace. A diamond cutter was used to obtain the cross-section of the crucible containing the sample and also to separate the alloy and slag physically. The physical separation approach involves separating the phases manually by applying slight pressure to the interface of the alloy and slag. An amount of 0.1 g of the quenched ground alloy was taken for chemical analysis to measure B and P concentration, using a similar digestion technique for the alloy described in Section 2.1. The final concentration of B and P was measured by ICP-OES.

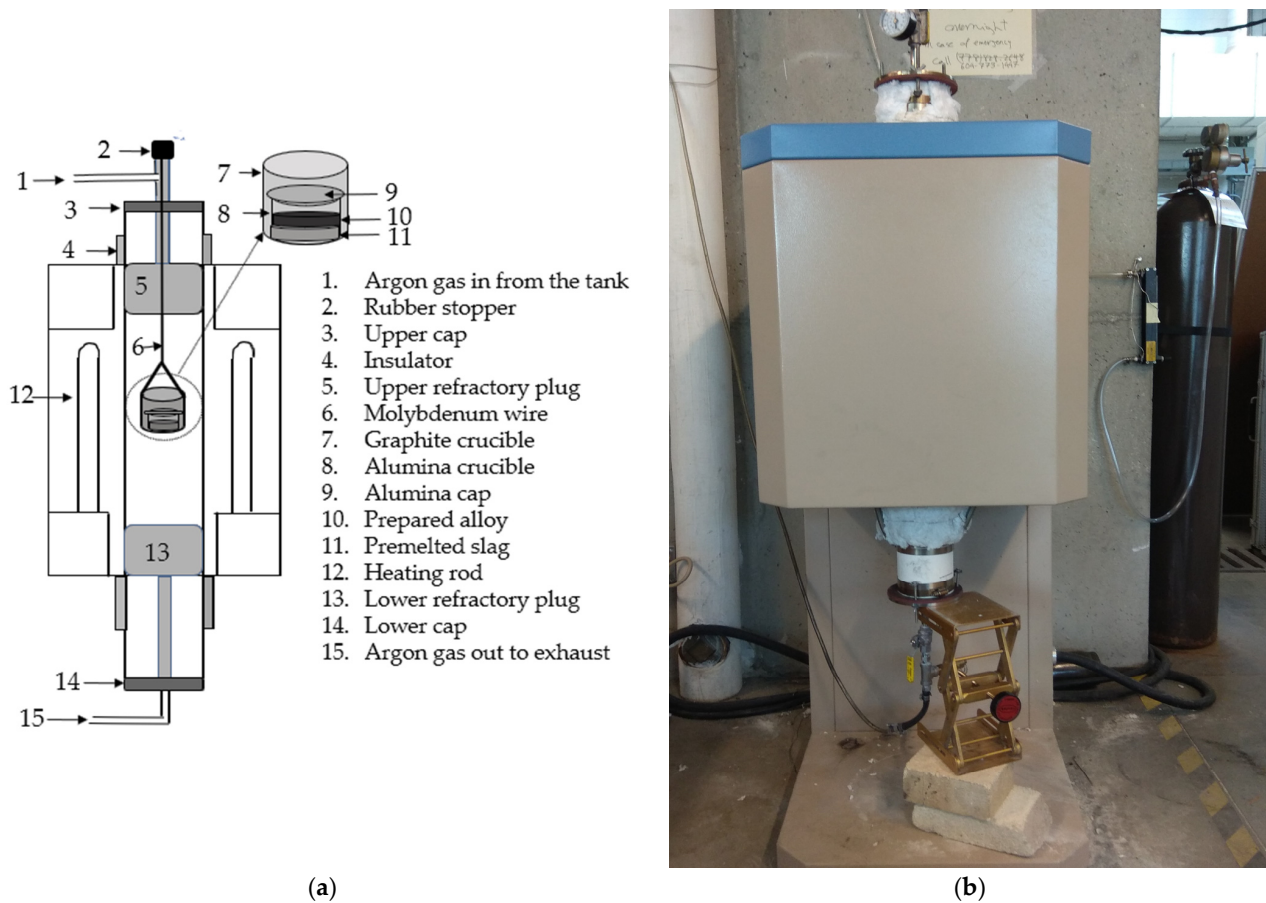


Figure 1. (a) Schematic and (b) physical image of the vertical tube furnace.

3. Results

3.1. Mass Transfer Control Kinetic Model

The removal of B and P from the alloy phase involves three steps. First is the transport of B and P in the alloy phase, the second is the oxidation and dissolution reactions at the interface, and the last step is the transport in the slag phase. The reactions at the interface are expected to be fast as the reaction temperature is 1300 °C. Therefore, it is logical to assume that the rate-controlling step should be the transport of B and P in the alloy or the slag phase. The results of the experimental work described above were used to find the rate-limiting steps for B and P.

Assuming a first-order reaction, the rate of change of the concentration of impurities, I ($I = B$ or P) in the alloy and slag phase, is given by Equations (1) and (2).

$$-\frac{d[I]}{dt} = \frac{A}{V_A} K_A ([I]_b - [I]_i) \quad (1)$$

$$\frac{d(I)}{dt} = \frac{A}{V_S} K_S ((I)_i - (I)_b) \quad (2)$$

Here, A stands for the slag–alloy interface area (m^2), V_A and V_S stand for the alloy and slag volumes (m^3), and $[I]$ and (I) stand for the impurities' concentrations (ppmw) in the alloy and slag phase, respectively. Interface and bulk are denoted by the subscripts “i” and “b”. The mass transfer coefficients (ms^{-1}) of impurities in the alloy and slag phases are K_A and K_S , respectively.

Considering the equilibrium condition of impurities' distribution at the interface of the alloy and slag phase, the partition ratio, L_I , which is the ratio of the impurity concentration

in slag to that of the alloy at equilibrium, i.e., $\frac{[I]_e}{[I]_i}$, can be written as the ratio of the impurity concentration at the interface, i.e., $\frac{[I]_i}{[I]_e}$ (Equation (3)).

$$L_I = \frac{[I]_i}{[I]_e} = \frac{[I]_e}{[I]_e} \quad (3)$$

The mass balance equation for impurity I is shown in Equation (4).

$$M_A[I]_0 + M_S(I)_0 = M_A[I] + M_S(I) \quad (4)$$

Here, M_A and M_S are the mass (g) of the alloy and slag, respectively. The subscription “0” stands for the initial state. Substituting Equations (3) and (4) into Equations (1) and (2) and integrating them with the initial conditions, $[I] = [I]_0$ and $(I) = (I)_0$, Equations (5) and (6) can be derived.

$$\frac{V_A}{A} \cdot \frac{M_A[I]_0 + M_S(I)_0 - M_A[I]_e}{M_A[I]_0 + M_S(I)_0} \cdot \ln \frac{[I] - [I]_e}{[I]_0 - [I]_e} = -K_A t \quad (5)$$

$$\frac{V_S}{A} \cdot \frac{M_A[I]_e}{M_A[I]_0 + M_S(I)_0} \cdot \ln \frac{[I] - [I]_e}{[I]_0 - [I]_e} = -K_S t \quad (6)$$

The derivations of the kinetic equations are available in [39]. For easier understanding, Equations (5) and (6) can be re-written as Equation (7).

$$Y_{A/S} \ln Z = -K_{A/S} t \quad (7)$$

Here, Z is $\frac{[I] - [I]_e}{[I]_0 - [I]_e}$ and $Y_{A/S}$ depends on the particular rate-determining step. That means, for the Si-Fe alloy phase, $Y_A = \frac{V_A}{A} \cdot \frac{M_A[I]_0 + M_S(I)_0 - M_A[I]_e}{M_A[I]_0 + M_S(I)_0}$, and for the slag, $Y_S = \frac{V_S}{A} \cdot \frac{M_A[I]_e}{M_A[I]_0 + M_S(I)_0} \cdot \ln \frac{[I] - [I]_e}{[I]_0 - [I]_e}$ is constant at any particular time. When $t = 0$, $[I] = [I]_0$; therefore, $Y_{A/S} \ln Z = 0$. As a result, the linear regression function must pass through the origin. The concentration of impurities in the alloy phase reduces with time. As the reaction proceeds, $[I]$ becomes smaller than $[I]_0$ and it continuously decreases. Therefore, $Y_{A/S} \ln Z$ has a negative value which decreases with time. This in turn results in the fitted regression line having a negative slope and $K_{A/S}$ having a positive value. The mass transfer coefficient, $K_{A/S}$, is the negative of the slope of the regression line fitted to the $Y_{A/S} \ln Z$ versus time (t) data. The rate-determining step can be determined by comparing K_A and K_S for B and P.

3.2. Interfacial Area of Alloy and Slag

The cross-section of the sample including the alloy and the slag phase is shown in Figure 2. Inside the alumina crucible, the slag phase surrounds the alloy as it takes on a spherical shape. The sphere's diameter is estimated to be 12 mm. The total surface area of the alloy sphere was calculated knowing its diameter. However, approximately 1/6 of the alloy surface area was uncovered by the slag. To determine the estimated interfacial area of the alloy and the slag for the kinetic study, the uncovered area was subtracted from the alloy's total area. The estimated interfacial area of the alloy and slag was 3.77 cm².

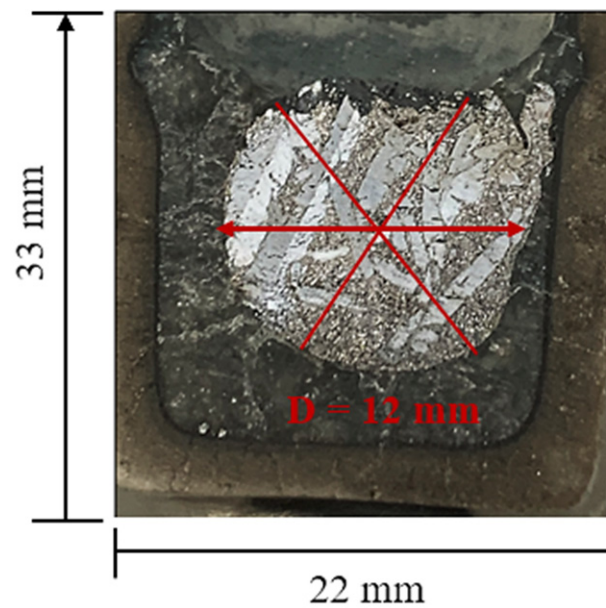


Figure 2. Cross-section of the quenched sample including the spherical alloy and the surrounding slag phase in an alumina crucible.

3.3. Kinetic Analysis of B Removal

Because full composition homogeneity is difficult to achieve, it was expected that there would be some variation in the initial concentration of B in different samples prior to the refining process. As a result, the initial impurity concentration of each sample was determined independently. The average of the initial concentration of B from three samples was taken for experimental analysis. The details of the measurement procedure of the initial B concentration in the alloy and the final concentration of B in the refined alloy were discussed in Section 2. The B concentration of each sample was determined using the average of these three measurements. The experimental results are tabulated in Table 1.

Table 1. Initial, final, and normalized concentration of B, $Y_A \ln Z$, and $Y_S \ln Z$ at 1300 °C.

Sample ID	Time (Hours)	Initial [B] _{Alloy} (ppmw)	Final [B] _{Alloy} (ppmw)	Normalized [B]	$Y_A \ln Z$	$Y_S \ln Z$
1	2	190.43	82.54	0.43	−0.51	−0.21
2	3	186.53	68.77	0.37	−0.68	−0.29
3	4	230.28	82.13	0.36	−0.72	−0.31
4	5	222.30	66.96	0.30	−1.33	−0.56
5	6	191.93	54.81	0.29	equilibrium	equilibrium
6	8	189.50	55.82	0.29	equilibrium	equilibrium

Normalized B concentration of the refined alloy to the initial concentration of each sample at different reaction times is shown in Figure 3. It is clear that B removal from the alloy was fast in the first 2 h of the process. As time increases, the concentration of B in the alloy phase decreases. The B transport reached the equilibrium state after 6 h of equilibrium time.

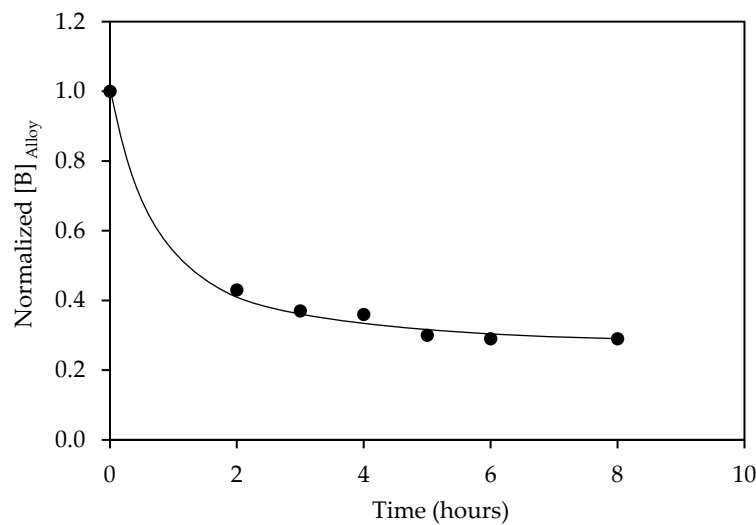


Figure 3. Normalized B concentration in the refined alloy vs. time at 1300 °C.

Based on the experimental results, B concentration after 6 h is chosen as the equilibrium concentration, $[B]_e$. The mass transfer coefficient of B in the alloy phase was calculated using the kinetic model described in Section 3.1. The $Y_A \ln Z$ values are plotted as a function of time in Figure 4. The mass transport coefficient of B in the alloy is determined from the slope of the linear regression fitted to the plotted data points. The K_A was found to be $6.6 \times 10^{-7} \text{ ms}^{-1}$. To the best of the authors' knowledge, the mass transfer coefficient of B in Si-20 wt% Fe has not previously been reported.

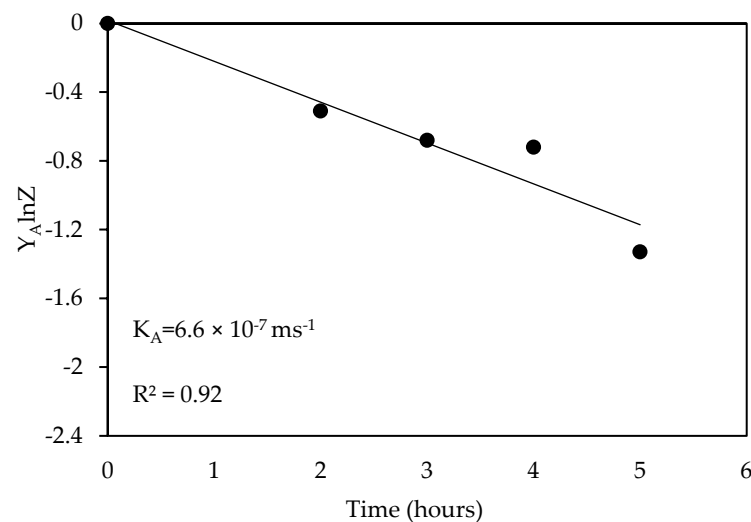


Figure 4. The $Y_A \ln Z$ vs. time for B mass transfer kinetics in the Si-20 wt% Fe.

The mass transfer coefficient of B in the slag phase was determined via a similar kinetic model. The acquired $Y_S \ln Z$ values versus time are plotted in Figure 5. The slope of the linear regression function is used to determine the mass transfer coefficient of B in the slag. The K_S was calculated to be $2.8 \times 10^{-7} \text{ ms}^{-1}$, which is less than the K_A of $6.6 \times 10^{-7} \text{ ms}^{-1}$. Therefore, it is concluded that B removal is governed by B mass transfer in the slag.

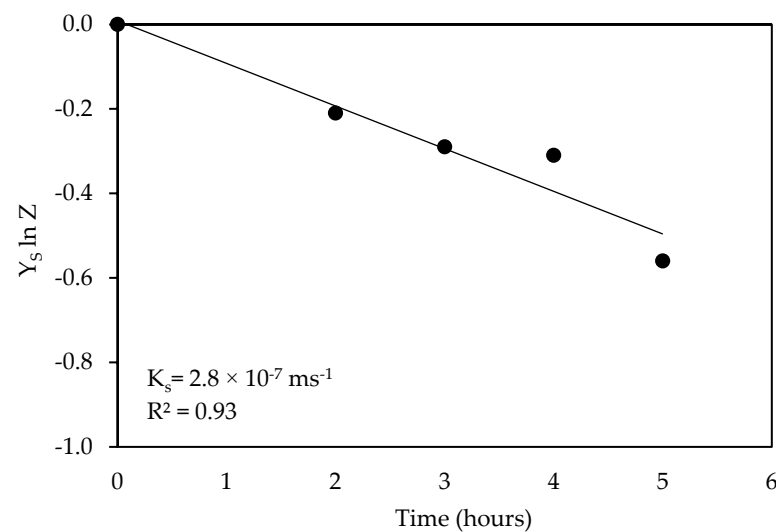


Figure 5. The $Y_S \ln Z$ vs. time for B mass transfer kinetics in the 45 wt% CaO–30 wt% SiO₂–15 wt% Al₂O₃–10 wt% Na₂O phase.

In a previous investigation, the mass transfer coefficients of B in the slag containing 46 wt% CaO–38.1 wt% SiO₂–15.9 wt% Al₂O₃ were determined to be $1.23 \times 10^{-6} \text{ ms}^{-1}$ at 1500 °C, $1.38 \times 10^{-6} \text{ ms}^{-1}$ at 1550 °C, and $1.83 \times 10^{-6} \text{ ms}^{-1}$ at 1600 °C [31]. In a different research study, Si metal was refined with 65 wt% Na₂O–35 wt% SiO₂ slag. The mass transfer coefficient of B in the slag at 1650 °C was found to be $5.8 \times 10^{-8} \text{ ms}^{-1}$ [40]. The current slag contains 45 wt% CaO–30 wt% SiO₂–15 wt% Al₂O₃–10 wt% Na₂O, and the mass transfer coefficient of B was found to be $2.8 \times 10^{-7} \text{ ms}^{-1}$.

In silicate slags, tetrahedral units of SiO₄^{4−} form when the Si⁴⁺ ion is surrounded by four O^{2−} ions [41–43]. Complex silicate networks are formed by these tetrahedral units in the form of chains, sheets, and 3D structures. Higher SiO₄^{4−} content of the slag typically results in higher polymerization which in turn leads to higher viscosity. Cations such as Ca²⁺ and Na⁺ are network breakers that hinder slag polymerization. Therefore, the presence of basic oxides such as CaO and Na₂O generally results in lower viscosity. Higher temperature also results in lower slag viscosity of silicate slag. Cations such as Al³⁺ can fit into the polymeric structure of the silicate slags. However, the charge balance needs to be maintained. For example, in the current study, a Na⁺ ion close to an Al³⁺ will play the charge-balancing role.

It has been shown that the temperature affects the mass transfer coefficient of boron in CaO–SiO₂ and CaO–SiO₂–Al₂O₃ slags [31]. Higher temperature results in lower viscosity that favors B transport and increases the mass transfer coefficient in the slag phase. The influence of molecular properties of silicate slags such as CaO–SiO₂–MgO was investigated using Raman spectroscopy [44]. The investigation reveals that the presence of CaO promotes B transport while MgO does not have an impact on B removal.

The ionic structure of slag affects its thermophysical properties. Similarly, B mass transfer value is directly influenced by the ionic structure of the slag phase. Current research is based on CaO–SiO₂–Al₂O₃–Na₂O quaternary slag which has a different ionic structure than the previous binary (Na₂O–SiO₂) and ternary slags (CaO–SiO₂–Al₂O₃). The reaction temperature in this investigation is also lower, 1300 °C, than the previous work. Thus, it is difficult to compare the current evaluated K_S value with the previous research. It might be concluded that the mass transfer coefficient depends on the ionic structure and the temperature of the slag. However, it would be prudent to conduct more refining experiments with the goal of increasing the mass transport coefficient of B in the slag.

3.4. Kinetic Analysis of P Removal

The initial concentration of P in the master alloy was determined using a similar method as B. The final concentration of P in the refined alloy and slag were also measured by ICP-OES analysis. The final concentration was later normalized with the average of the three initial concentrations of the samples. The experimental findings, $Y_A \ln Z$, and $Y_S \ln Z$ are shown in Table 2.

Table 2. Initial, final, and the normalized concentration of P, $Y_A \ln Z$, and $Y_S \ln Z$ at 1300 °C.

Sample No	Time (Hours)	Initial [P] _{Alloy} (ppmw)	Final [P] _{Alloy} (ppmw)	Normalized [P]	$Y_A \ln Z$	$Y_S \ln Z$
1	2	224.30	213.54	0.95	−0.03	−0.12
2	3	178.10	159.60	0.90	−0.06	−0.30
3	4	232.20	204.00	0.88	−0.09	−0.41
4	5	178.90	150.90	0.84	−0.17	−0.82
5	6	189.35	155.70	0.82	equilibrium	equilibrium
6	8	172.45	140.99	0.82	equilibrium	equilibrium

The normalized value indicates the change in the concentration of P in the refined alloy with respect to time as shown in Figure 6. As time increases, the concentration of P decreases and reaches the equilibrium state after 6 h. However, the change in P concentration was not as significant as B.

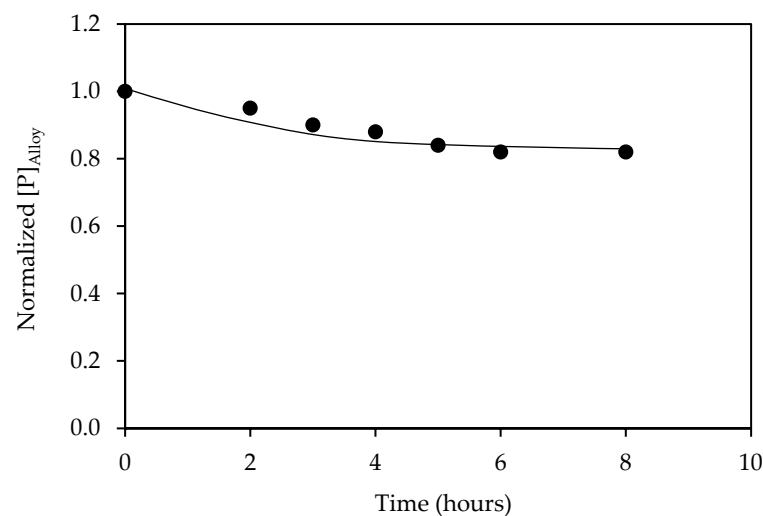


Figure 6. Normalized P concentration in the refined alloy vs. reaction time at 1300 °C.

The first-order kinetic model was implemented to find the mass transfer coefficient value for P in the alloy phase at 1300 °C. The $Y_A \ln Z$ values were calculated and shown in Figure 7. The mass transfer coefficient value of P in the alloy phase was determined using the slope of the linear regression line. The mass transfer coefficient of P in the Si-20 wt% Fe alloy was found to be $7.5 \times 10^{-8} \text{ ms}^{-1}$ at 1300 °C.

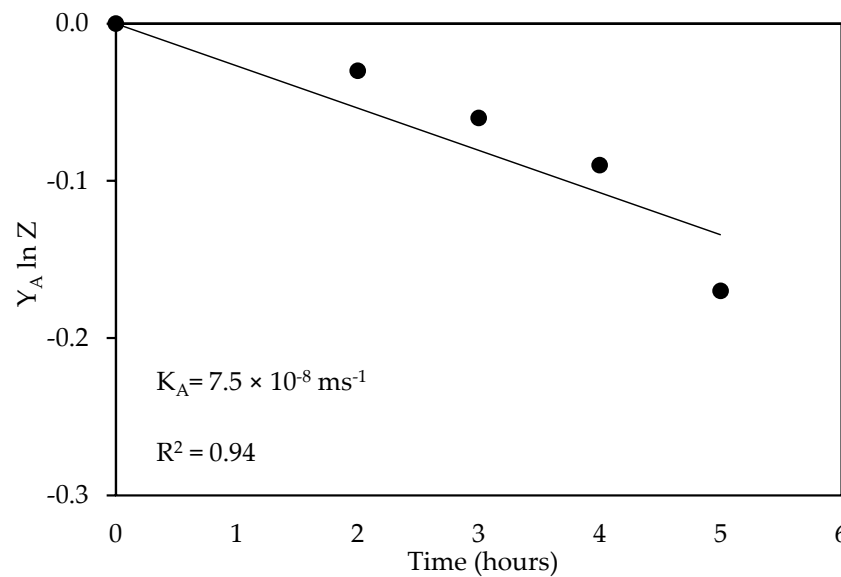


Figure 7. The $Y_A \ln Z$ plot vs. time for P mass transfer kinetics in the Si–20 wt% Fe phase.

The mass transfer coefficient of P in the slag phase was also calculated using a similar kinetic model. The estimated $Y_S \ln Z$ with respect to time is plotted in Figure 8. The data points are fitted to a linear regression function as illustrated in the aforementioned figure. The mass transfer coefficient in the slag was calculated using the slope of the regression line. The mass transfer coefficient of P in the quaternary slag of CaO–SiO₂–Al₂O₃–Na₂O was found to be $3.5 \times 10^{-7} \text{ ms}^{-1}$ at 1300 °C. The mass transfer coefficient in slag, K_S , for P is greater than the mass transfer coefficient of P in the alloy phase, K_A , indicating that P transfer in the alloy is the rate-limiting step for P removal in refining Si-20 wt% Fe alloy with CaO–SiO₂–Al₂O₃–Na₂O slag at 1300 °C.

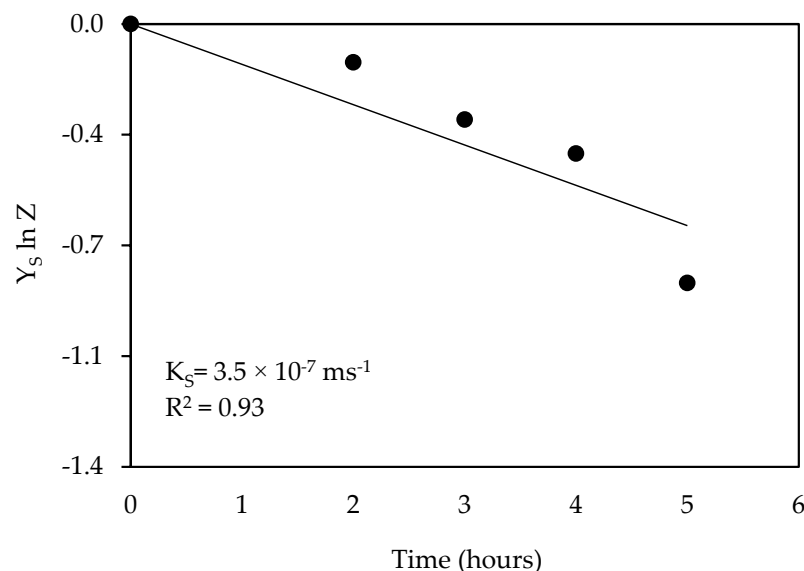


Figure 8. The $Y_S \ln Z$ vs. time of P mass transfer kinetics in the 45 wt% CaO–30 wt% SiO₂–15 wt% Al₂O₃–10 wt% Na₂O phase.

The findings of a previous work on the Si–Cu refining process with CaO–SiO₂–CaCl₂ slag at 1550 °C determined the P mass transfer coefficient in the slag to be $2.55 \times 10^{-6} \text{ ms}^{-1}$ [45]. This value is approximately an order of magnitude higher than the P mass transport coefficient which was found in the current study. The difference is most likely attributed to the variation

in slag composition and temperature. The data on the mass transfer of P in Si or Si alloy is extremely scarce. The P mass transfer coefficient in Si-20 wt% Fe is obtained based on the experimental results of the current investigation. However, further research should be conducted to examine the mass transfer coefficient of P in other Si alloys as well as the slags, particularly to correlate the P mass transfer coefficient to the slag physiochemical characteristics and ionic structure.

4. Conclusions

The kinetic analyses of B and P removal from Si-20 wt% Fe alloy have been carried out using a quaternary slag of 45 wt% CaO-30 wt% SiO₂-15 wt% Al₂O₃-10 wt% Na₂O at 1300 °C. The normalized B concentration in the refined alloy phase showed a relatively high B removal rate at the beginning of the refining process. The removal rate gradually drops, resulting in the equilibrium state in 6 h. The mass transfer coefficient for B in the alloy phase was found to be $6.6 \times 10^{-7} \text{ ms}^{-1}$ and in the slag phase it was $2.8 \times 10^{-7} \text{ ms}^{-1}$. Therefore, it was concluded that B distribution between the alloy and the slag was controlled by the B transport in the slag phase. On the other hand, the P removal rate from the alloy was relatively small and P concentration reached the equilibrium state after 6 h of reaction time. The P mass transfer coefficient values in the alloy and slag phase were determined to be $7.5 \times 10^{-8} \text{ ms}^{-1}$ and $3.5 \times 10^{-7} \text{ ms}^{-1}$, respectively. Therefore, it was concluded that P transport in the alloy phase is slower than the slag phase, resulting in the P transfer in the alloy being the rate-limiting step for P removal. In summary, comparing the mass transfer coefficients of B in the alloy and the slag, the rate-limiting step for B removal was found to be the B transport in the slag phase. However, the rate-limiting step for P was P transfer in the alloy. The findings provide evidence for the mechanisms of the removal of B and P from Si-Fe alloy.

Author Contributions: Conceptualization, L.T.K.; methodology, L.T.K. and G.I.A.T.; software, G.I.A.T.; validation, L.T.K. and G.I.A.T.; formal analysis, G.I.A.T.; investigation, L.T.K. and G.I.A.T.; resources, L.T.K.; data curation, G.I.A.T.; writing—original draft preparation, G.I.A.T.; writing—review and editing, L.T.K.; visualization, L.T.K. and G.I.A.T.; supervision, L.T.K.; project administration, L.T.K.; funding acquisition, L.T.K. All authors have read and agreed to the published version of the manuscript.

Funding: The present work has been partially supported by the Natural Sciences and Engineering Research Council of Canada (NSERC, RGPIN-2017-04669).

Data Availability Statement: Data contained in the article are available in Tables 1 and 2.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Johnston, M.D.; Khajavi, L.T.; Li, M.; Sokhanvaran, S.; Barati, M. High-temperature refining of metallurgical-grade silicon: A review. *JOM* **2012**, *64*, 935–945. [\[CrossRef\]](#)
2. Johnston, M.; Barati, M. Distribution of impurity elements in slag-silicon equilibria for oxidative refining of metallurgical silicon for solar cell applications. *Sol. Energy Mater. Sol. Cells* **2010**, *94*, 2085–2090. [\[CrossRef\]](#)
3. Hosseinpour, A.; Tafaghodi Khajavi, L. Slag refining of silicon and silicon alloys: A review. *Miner. Process. Extr. Metall. Rev.* **2018**, *39*, 308–318. [\[CrossRef\]](#)
4. Thomas, S.; Barati, M.; Morita, K. A review of slag refining of silicon alloys. *JOM* **2021**, *73*, 282–292. [\[CrossRef\]](#)
5. Serikkanov, A.; Pavlov, A.; Mukashev, B.; Turmagambetov, T.; Kantarbayeva, D.; Zholdybayev, K. The Possibility of Silicon Purification by Metallurgical Methods: Part I. *Processes* **2022**, *10*, 1353. [\[CrossRef\]](#)
6. Teixeira, L.A.V.; Tokuda, Y.; Yoko, T.; Morita, K. Behavior and state of boron in CaO-SiO₂ slags during refining of solar grade silicon. *ISIJ Int.* **2009**, *49*, 777–782. [\[CrossRef\]](#)
7. Jakobsson, L.K.; Tangstad, M. Distribution of boron between silicon and CaO-MgO-Al₂O₃-SiO₂ slags. *Metall. Mater. Trans. B* **2014**, *45*, 1644–1655. [\[CrossRef\]](#)
8. Safarian, J.; Tranell, G.; Tangstad, M. Thermodynamic and kinetic behavior of B and Na through the contact of B-doped silicon with Na₂O-SiO₂ slags. *Metall. Mater. Trans. B* **2013**, *44*, 571–583. [\[CrossRef\]](#)
9. Al-khazraji, R.; Li, Y.-q.; Zhang, L.-f. Boron separation from Si-Sn alloy by slag treatment. *Int. J. Miner. Metall. Mater.* **2018**, *25*, 1439–1446. [\[CrossRef\]](#)

10. Li, J.; Zhang, L.; Tan, Y.; Jiang, D.; Wang, D.; Li, Y. Research of boron removal from polysilicon using CaO–Al₂O₃–SiO₂–CaF₂ slags. *Vacuum* **2014**, *103*, 33–37. [\[CrossRef\]](#)
11. Yoshikawa, T.; Morita, K. Removal of B from Si by solidification refining with Si–Al melts. *Metall. Mater. Trans. B* **2005**, *36*, 731–736. [\[CrossRef\]](#)
12. Yoshikawa, T.; Morita, K. Refining of Si by the solidification of Si–Al melt with electromagnetic force. *ISIJ Int.* **2005**, *45*, 967–971. [\[CrossRef\]](#)
13. Yoshikawa, T.; Morita, K. Continuous solidification of Si from Si–Al melt under the induction heating. *ISIJ Int.* **2007**, *47*, 582–584. [\[CrossRef\]](#)
14. Yoshikawa, T.; Arimura, K.; Morita, K. Boron removal by titanium addition in solidification refining of silicon with Si–Al melt. *Metall. Mater. Trans. B* **2005**, *36*, 837–842. [\[CrossRef\]](#)
15. Yoshikawa, T.; Morita, K. Removal of phosphorus by the solidification refining with Si–Al melts. *Sci. Technol. Adv. Mater.* **2003**, *4*, 531–537. [\[CrossRef\]](#)
16. Mitrašinović, A.M.; Utigard, T.A. Refining silicon for solar cell application by copper alloying. *Silicon* **2009**, *1*, 239–248. [\[CrossRef\]](#)
17. Mitrašinović, A. Characterization of the Cu–Si System and Utilization of Metallurgical Techniques in Silicon Refining for Solar Cell Applications. Ph.D. Thesis, Department of Materials Science and Engineering, University of Toronto, Toronto, ON, Canada, 2010.
18. Khajavi, L.T.; Morita, K.; Yoshikawa, T.; Barati, M. Thermodynamics of boron distribution in solvent refining of silicon using ferrosilicon alloys. *J. Alloys Compd.* **2015**, *619*, 634–638. [\[CrossRef\]](#)
19. Tafaghodi Khajavi, L.; Barati, M. Thermodynamics of phosphorus in solvent refining of silicon using ferrosilicon alloys. *Metall. Mater. Trans. B* **2017**, *48*, 268–275. [\[CrossRef\]](#)
20. Khajavi, L.T.; Barati, M. Thermodynamics of phosphorus removal from silicon in solvent refining of silicon. *High Temp. Mater. Process.* **2012**, *31*, 627–631. [\[CrossRef\]](#)
21. Thomas, S.; Huang, L.; Barati, M. A Review of Slag Refining of Crude Silicon. *JOM* **2020**, *73*, 260–281. [\[CrossRef\]](#)
22. Taposhe, G.I.A.; Khajavi, L.T. Removal of phosphorus from Si–Fe alloy by CaO–Al₂O₃–SiO₂–Na₂O slag refining. *JOM* **2021**, *73*, 729–735. [\[CrossRef\]](#)
23. Taposhe, G.I.A.; Khajavi, L.T. Thermodynamics of Impurities Removal from Si–Fe Alloy by CaO–Al₂O₃–SiO₂–Na₂O Slag Refining. *Metall. Mater. Trans. B* **2022**, *53*, 4019–4028. [\[CrossRef\]](#)
24. Hosseinpour, A.; Tafaghodi Khajavi, L. Phosphorus removal from Si–Fe alloy using SiO₂–Al₂O₃–CaO slag. *Metall. Mater. Trans. B* **2019**, *50*, 1773–1781. [\[CrossRef\]](#)
25. Hosseinpour, A.; Khajavi, L.T. Thermodynamics of boron removal in slag refining of Fe–Si alloy. *J. Alloys Compd.* **2018**, *768*, 545–552. [\[CrossRef\]](#)
26. Li, M.; Utigard, T.; Barati, M. Removal of boron and phosphorus from silicon using CaO–SiO₂–Na₂O–Al₂O₃ flux. *Metall. Mater. Trans. B* **2014**, *45*, 221–228. [\[CrossRef\]](#)
27. Ma, X.; Yoshikawa, T.; Morita, K. Purification of metallurgical grade Si combining Si–Sn solvent refining with slag treatment. *Sep. Purif. Technol.* **2014**, *125*, 264–268. [\[CrossRef\]](#)
28. Ma, X.; Yoshikawa, T.; Morita, K. Removal of boron from silicon–tin solvent by slag treatment. *Metall. Mater. Trans. B* **2013**, *44*, 528–533. [\[CrossRef\]](#)
29. Krystad, E.; Tang, K.; Tranell, G. The kinetics of boron transfer in slag refining of silicon. *JOM* **2012**, *64*, 968–972. [\[CrossRef\]](#)
30. Krystad, E.; Jakobsson, L.K.; Tang, K.; Tranell, G. Thermodynamic Behavior and Mass Transfer Kinetics of Boron between Ferrosilicon and CaO–SiO₂ Slag. *Metall. Mater. Trans. B* **2017**, *48*, 2574–2582. [\[CrossRef\]](#)
31. Islam, M.; Rhamdhani, M. Kinetics Analysis of Boron Removal from Silicon through Reactions with CaO–SiO₂ and CaO–SiO₂–Al₂O₃ Slags. *Metall. Mater. Trans. B* **2018**, *49*, 3171–3185. [\[CrossRef\]](#)
32. Zhang, L.; Tan, Y.; Li, J.; Liu, Y.; Wang, D. Study of boron removal from molten silicon by slag refining under atmosphere. *Mater. Sci. Semicond. Process.* **2013**, *16*, 1645–1649. [\[CrossRef\]](#)
33. Nishimoto, H.; Kang, Y.; Yoshikawa, T.; Morita, K. The rate of boron removal from molten silicon by CaO–SiO₂ slag and Cl₂ treatment. *High Temp. Mater. Process.* **2012**, *31*, 471–477. [\[CrossRef\]](#)
34. Bjerke, H. Removal of Boron from Silicon by Slag Treatment and by Evaporation of Boron from Slag in Hydrogen Atmosphere. Master's Thesis, Institutt for Materialteknologi, Norwegian University of Science and Technology, Trondheim, Norway, 2012.
35. Li, Y.; Wu, J.; Ma, W.; Yang, B. Boron removal from metallurgical grade silicon using a refining technique of calcium silicate molten slag containing potassium carbonate. *Silicon* **2015**, *7*, 247–252. [\[CrossRef\]](#)
36. Lu, C.; Huang, L.; Lai, H.; Fang, M.; Ma, W.; Xing, P.; Zhang, L.; Li, J.; Luo, X. Effects of slag refining on boron removal from metallurgical-grade silicon using recycled slag with active component. *Sep. Sci. Technol.* **2015**, *50*, 2759–2766. [\[CrossRef\]](#)
37. Wu, J.; Wang, F.; Ma, W.; Lei, Y.; Yang, B. Thermodynamics and kinetics of boron removal from metallurgical grade silicon by addition of high basic potassium carbonate to calcium silicate slag. *Metall. Mater. Trans. B* **2016**, *47*, 1796–1803. [\[CrossRef\]](#)
38. Lai, H.; Huang, L.; Lu, C.; Fang, M.; Ma, W.; Xing, P.; Li, J.; Luo, X. Reaction mechanism and kinetics of boron removal from metallurgical-grade silicon based on Li₂O–SiO₂ slags. *JOM* **2016**, *68*, 2371–2380. [\[CrossRef\]](#)
39. Engh, T. *Principles of Metal Refining*; Oxford University Press: Oxford, UK, 2021; p. 259.
40. Huang, L.; Chen, J.; Fang, M.; Thomas, S.; Danaei, A.; Luo, X.; Barati, M. Clean enhancing elimination of boron from silicon kerf using Na₂O–SiO₂ slag treatment. *J. Clean. Prod.* **2018**, *186*, 718–725. [\[CrossRef\]](#)
41. Mysen, B.O.; Mysen, B. *Structure and Properties of Silicate Melts*; Elsevier: Amsterdam, The Netherlands, 1988; Volume 354.

42. Mills, K.C. The influence of structure on the physico-chemical properties of slags. *ISIJ Int.* **1993**, *33*, 148–155. [[CrossRef](#)]
43. Mysen, B.O. Relationships between silicate melt structure and petrologic processes. *Earth-Sci. Rev.* **1990**, *27*, 281–365. [[CrossRef](#)]
44. Krystad, E.; Kline, J.; Tangstad, M.; Tranell, G. The relationship between silicate structure and mass transfer of boron in slag refining of silicon. In Proceedings of the 9th International Conference on Molten Slags, Fluxes and Salts (MOLTEN12), Beijing, China, 27–30 May 2012.
45. Huang, L.; Lai, H.; Gan, C.; Xiong, H.; Xing, P.; Luo, X. Separation of boron and phosphorus from Cu-alloyed metallurgical grade silicon by CaO–SiO₂–CaCl₂ slag treatment. *Sep. Purif. Technol.* **2016**, *170*, 408–416. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.